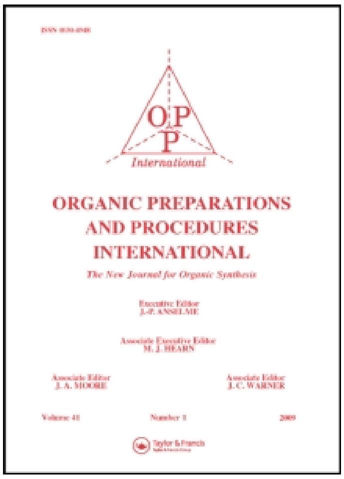

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2,3-DIAZABICYCLO[2.2.1]-2-HEPTENE M-OXIDE

Robert C. Kerber[a]; Thomas J. Ryan[a]
[a] Department of Chemistry, State University of New York, Stony Brook, New York

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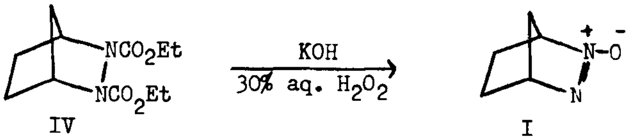
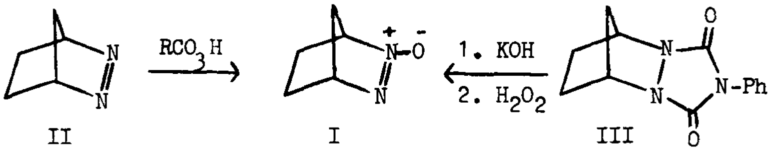
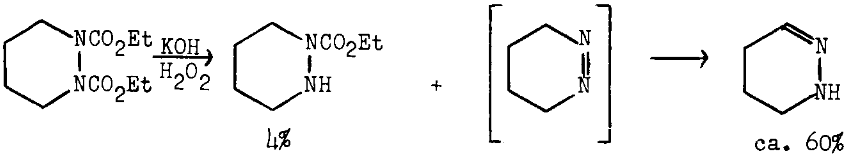


The title compound, I, has recently been prepared (a) by oxidation of the corresponding azo compound, II, with m-chloroperbenzoic acid[1] and (b) by hydrolysis of the triazolidinedione, III, followed by peroxide oxidation of the resulting hydrolysate.[2]



Route (a) suffers from its many steps and from the relatively low yield (36%) of azo compound II obtained from IV. Route (b) requires the preparation of 4-phenylurazole and its in situ oxidation to give the reactive dienophile 4-phenyl-1,2,4-triazoline-3,5-dione (V).[3]

We here report that **I** can be prepared directly from **IV** which can in turn be obtained essentially quantitatively from commercially available starting materials.[3] This provides a very convenient route to **I** and possibly to other bicyclic azoxy compounds.[4] However no azoxy compound is obtained from diethyl hexahydropyridazine-1,2-dicarboxylate, due to rapid tautomerization of the intermediate azo compound.[6]



EXPERIMENTAL

Diethyl 2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate, **IV**, (9.70 g, 0.04 mole) was suspended in 200 ml of 30% aq. hydrogen peroxide in a 1 ℓ three-necked flask fitted with mechanical stirrer, reflux condenser, and dropping funnel. The mixture was cooled in an ice bath, and a solution of 24 g (0.6 mole) of sodium hydroxide in 100 ml of water was added dropwise, while the solution was stirred. One half hour after addition was complete the reaction mixture was stirred for an additional 12 hours at 45° (water bath). It was then extracted with three 50 ml portions of methylene chloride, and the organic layer dried over $MgSO_4$. Evaporation of the solvent left a residue which was pressed on filter paper and dried over KOH, giving 2.43 g (54%) of crude **1** as a white solid, mp. 85-93°. The material could be purified by sublimation at 75°/15 mm, to give the pure product as white powder, mp 89-91°, lit.[1,2] mp. 87-89°, 93-95°. Its spectral data (IR,nmr) agreed with those previously reported.[1,2]

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5. The tendency of diethyl azodicarboxylate, unlike V, to give side-reactions with many dienes limits the extension of this synthesis to some degree. For a number of cases of such side reactions, see Ref. 4a, and E. Fahr and H. Lind, Angew. Chem. Internat. Ed., 5, 372 (1966).
6. We are indebted to Miss Sou-Mei Yu for performing this experiment.
7. The compound is quite hygroscopic.

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